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(54) Title: PROCESS FOR COATING A SUBSTRATE WITH TITANIUM DIOXIDE

(57) Abstract

A process for coating a substrate surface with titanium dioxide, which process comprises the D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises sub-stoichiometric titanium dioxide, TiO<sub>x</sub>, where x is below 2.

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## PROCESS FOR COATING A SUBSTRATE WITH TITANIUM DIOXIDE

The present invention relates to an improved  
5 process for coating a substrate surface with titanium  
dioxide.

Sputtered coatings of various oxides (e.g.  
silica) and nitrides (e.g. silicon nitride) are used  
to form optical coatings showing interesting  
10 properties on a number of substrates. Known  
applications include low emissivity films on window  
glasses, cold mirrors on reflectors, enhanced mirrors  
for photocopiers and anti-reflective coatings on  
picture glass or TV screens. These coatings are  
15 usually made of stacks of several different layers  
with different refractive indices, preferably of low  
and high refractive index, to produce optical filters.  
For anti-reflective coatings it is preferred to  
combine two materials showing the highest and the  
20 lowest possible refractive indices. Such materials  
are titania and silica. Another advantage of these  
materials is their durability. For low emissivity  
films on window glasses it is preferred to combine a  
silver layer with a high refractive index material to  
25 dereflect the silver which improves light  
transmission.

Titanium dioxide coatings have a high refractive  
index and can thus be used to provide coatings of a  
high refractive index or to provide the high  
30 refractive index coatings in optical stacks. The  
existing process for producing titanium dioxide  
coatings comprises using titanium metal as the  
sputtering target and using oxygen as a component of  
the plasma gas. The titanium is thus converted to  
35 titanium dioxide during the sputtering process.

Although satisfactory coatings of titanium dioxide can be produced, the rate of deposition is very slow and much slower than coating with zinc oxide and/or tin oxide. The stability of the sputtering process and the arc rate are both very dependent upon the conductivity of the target, particularly at high power levels.

As a substitute for titanium dioxide it has been suggested to use alternative materials such as niobium oxide. Whilst it is possible to coat a substrate with niobium oxide using a niobium metal target at slightly higher speeds than the equivalent process using titanium, niobium is very expensive.

JP-A-62-161945 describes a method of manufacturing a ceramic sputtering target in which a ceramic material consisting mainly of  $ZrO_2$ ,  $TiO_2$ ,  $SiO_2$ ,  $Ta_2O_3$ ,  $Al_2O_3$ ,  $Fe_2O_3$  or a compound of these materials, is sprayed using a water plasma spray to produce a formed body which may be used as a sputtering target. The sputtering target is used for high frequency sputtering of non-conductive target material.

JP-A-1-118807 describes a method for manufacturing titanium oxide thin films in which a target comprising titanium, titanium monoxide ( $TiO$ ), or titanium dioxide ( $TiO_2$ ) is used as a sputtering target and the target sputtered in a mixture of argon and oxygen using high frequency power density for example of 500W.

There is, however, still a need for an improved process for coating titanium dioxide onto substrate materials. We have now surprisingly discovered that titanium dioxide can be sputtered from a target comprising sub-stoichiometric titanium dioxide of low resistivity of less than 1 ohm.cm, preferably less than 0.1 ohm.cm to provide coatings on a substrate either of sub-stoichiometric titanium dioxide, or

titanium dioxide, depending upon the sputtering conditions.

Accordingly, the present invention provides a process for coating a substrate surface with titanium dioxide, which process comprises the D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises sub-stoichiometric titanium dioxide,  $TiO_x$ , where  $x$  is below 2, and which has a resistivity of below 1 ohm.cm.

Sub-stoichiometric titanium dioxide,  $TiO_x$ , where  $x$  is below 2 and generally is in the range of from 1.55 to 1.95 is known in the art. It is a form of titanium dioxide which is conductive. Preferably the sub-stoichiometric titanium dioxide used in the present invention has a resistivity of below 0.1 ohm.cm.

The sputtering target which is used in the process of the present invention comprises sub-stoichiometric titanium dioxide,  $TiO_x$  coated onto a target base, such as a backing tube or plate, for example a target base of an electrically conductive material, for example stainless steel or titanium metal, aluminium or copper. Because the sub-stoichiometric titanium dioxide is conductive, D.C. plasma sputtering and/or mid-frequency sputtering, such as the Twin-Mag System may be used. D.C. plasma sputtering is, however, preferred. The target may be of any type known in the art, for example a rotatable target or a flat magnetron target.

The sputtering target used in the process of the present invention may be prepared by plasma spraying titanium dioxide, optionally together with niobium oxide, onto a target base in an atmosphere which is oxygen deficient and which does not contain oxygen-containing compounds, the target base being coated

with  $\text{TiO}_x$ , where  $x$  is below 2, which is solidified under conditions which prevent the sub-stoichiometric titanium oxide from combining with oxygen. During the plasma spraying process, the action of the plasma on the titanium dioxide causes the titanium dioxide to lose some oxygen atoms from its lattice preferably from the surface of the particles. The titanium dioxide is converted into the sub-stoichiometric form, i.e. non-stoichiometric oxygen deficient titania

The sputtering from the sub-stoichiometric titanium dioxide,  $\text{TiO}_x$  target is preferably carried out using as the plasma gas argon, a mixture of argon and oxygen, a mixture of nitrogen and argon, or a mixture of nitrogen and oxygen. If the plasma gas does not contain oxygen, e.g. if pure argon is used, then the coating will comprise sub-stoichiometric titanium dioxide. The coating obtained is not completely transparent and possesses some conductivity. If, however, the plasma gas contains oxygen then the sub-stoichiometric form of titanium dioxide is converted during the sputtering process into the transparent form which is stoichiometric or substantially stoichiometric and has a high refractive index. The degree of transparency will depend upon the amount of oxygen contained in the plasma gas. A preferred gas mixture to form transparent titanium dioxide as the coating comprises 70-90% by volume argon and 30-10% by volume of oxygen.

The substrate which is coated according to this process may comprise, for example, optical glass, the screen of a cathode ray tube, such as a TV screen, cold mirrors, low-emissivity glasses, architectural glasses, anti-reflective panels, or flexible films such as oxygen barrier films.

The use of the target of the present invention

avoids any avalanche effect of titania towards the metallic state or poisoned oxygen state. There is no need for a sophisticated gas control system or plasma monitoring equipment. The target can be easily  
5 operated and controlled to produce stoichiometric or non-stoichiometric films of any level of sub-stoichiometry. By operating the target in a slightly oxygen deficient sputtering process, a high refractive index film can be obtained which is important for  
10 optical coatings. Depending on the sputtering parameters, amorphous or crystalline films can be formed with a rutile or anatase structure. Rutile films have improved optical, mechanical and electrical properties. When the sub-stoichiometric titanium  
15 dioxide is sputtered under conditions such that the coating is formed comprises stoichiometric titanium dioxide, the coating is essentially transparent and colourless.

Although films coated with stoichiometric  
20 titanium dioxide, for example for use in the packaging industry, have good oxygen barrier properties, they are statically loaded which is particularly disadvantageous especially for the packaging of powdered products, such as coffee.

25 When the coating formed from the sub-stoichiometric titanium dioxide sputtering targets is also sub-stoichiometric titanium dioxide, it has a reduced transparency and slightly blue colour but is conductive and thus possesses anti-static properties  
30 having an electrical resistivity of above  $3 \times 10^5$  ohm.cm. Accordingly, films coated with non-stoichiometric titanium dioxide not only have good oxygen barrier properties, but also possess particularly good anti-static properties which makes  
35 them particularly suitable for packaging applications,

particularly in the food industry. A further advantage of films coated with sub-stoichiometric titanium dioxide is that the coatings possess good flexibility which even after excessive bending and creasing retain their oxygen barrier properties. Although the films have a slight blue colour this does not detract from the potential use of the product in the food industry, the blue colour providing a "fresh" look to the product. As barrier films for water vapour and oxygen, there is an improvement when compared with the prior art titanium dioxide coated films of five fold for water vapour and three fold for oxygen.

The main advantage of the present invention is that from the sub-stoichiometric titanium dioxide targets used in the present invention the rate of sputtering is increased by a factor of about ten as compared to sputtering from a titanium metal target, thus making the process industrially attractive. Furthermore, the sputtering process is very stable with little or no arcing occurring.

The present invention will be further described with reference to the following Examples.

#### EXAMPLE 1 (Comparative)

A rotatable target comprising a tube of titanium metal of diameter 133mm and length 800mm was used to sputter titanium metal onto a glass plate placed at a distance of 18cm from the target. The sputtering was carried out at a power level of 35kW (80A, 446V) under a pressure of  $5 \times 10^{-3}$  mBar of argon as the plasma gas.

After  $3\frac{1}{2}$  minutes a layer of titanium metal 18000 Angstroms in thickness as measured by a profilometer had been deposited upon the glass plate.



EXAMPLE 2 (Comparative)

The procedure of Example 1 was repeated but substituting a mixture of 80%  $O_2$  and 20% Ar as the primary plasma gas to replace the argon primary plasma gas of Example 1. The sputtering was carried out at a power level of 45kW (97A, 460V) under a pressure of  $4.5 \times 10^{-3}$  mBar. Using a titanium metal target as described in Example 1 a titanium dioxide layer of thickness 1500 Angstroms was deposited on a glass plate placed above the target in  $3\frac{1}{2}$  minutes.

EXAMPLE 3

A rotatable target comprising a tube of stainless steel of diameter 133mm and length 800mm was coated with sub-stoichiometric titanium dioxide,  $TiO_x$ , where x is below 2 as hereinbefore described by plasma spraying titanium dioxide onto the target using argon as the primary plasma gas and hydrogen as the secondary plasma gas. 72 litres (60% argon, 40% hydrogen) were used. The power level was 45kW (455A, 96V).

This target was then used as a sputtering target in the manner as described in Example 1. Using argon as the primary plasma gas the sputtering was carried out at a power level of 45kW (97A, 460V) under a pressure of  $5.4 \times 10^{-3}$  mBar Ar. A dark blue semi-transparent layer of sub-stoichiometric titanium dioxide,  $TiO_x$ , of thickness 14000 Angstroms was deposited on a glass plate placed above the target in  $3\frac{1}{2}$  minutes. The sputtering proceeded smoothly without significant arcing.

**EXAMPLE 4**

A rotatable target prepared as described in Example 3 was used as a sputtering target in the manner as described in Example 3 using a mixture of 75% Ar and 25% O<sub>2</sub> as the plasma gas. The sputtering was carried out at a power of 45kW (95A, 473V) under a pressure of  $5 \times 10^{-3}$  mBar. A clear transparent coating of stoichiometric titanium dioxide of thickness 12500 Angstroms was deposited on a glass plate placed above the target in 3½ minutes. The sputtering proceeded smoothly without significant arcing.

**EXAMPLE 5 (Comparative)**

A rotatable target was prepared as described in Example 3 by using pure argon (40 litres) at a power level of 34 kW (820A, 42V). The electrical conductivity of the target was ten times inferior to that of Example 3. Sputtering from the target was difficult due to arcing. The process was not stable enough to produce samples.

**CLAIMS:**

1. A process for coating a substrate surface with titanium dioxide, which process comprises the  
5 D.C. plasma sputtering and/or mid-frequency sputtering from a sputtering target which comprises substoichiometric titanium dioxide,  $\text{TiO}_x$ , where x is below 2 and which has a resistivity of below 1 ohm.cm.

10 2. A process as claimed in claim 1 wherein the sputtering from the target is carried out using as the plasma gas argon, or a mixture of argon and nitrogen, whereby the coating formed on the substrate surface comprises sub-stoichiometric titanium dioxide,  $\text{TiO}_x$ ,  
15 where x is below 2.

3. A process as claimed in claim 1 wherein the sputtering for the target is carried out using as the plasma gas a mixture of argon and oxygen, or a mixture  
20 of nitrogen and oxygen, whereby the coating formed on the substrate surface comprises stoichiometric or substantially stoichiometric titanium dioxide.

4. A process as claimed in claim 3 wherein the  
25 plasma gas comprises 70 to 90% by volume argon and 30 to 10% by volume oxygen.

5. A process as claimed in any one of claims 1 to 4 wherein the substrate which is coated is optical  
30 glass, the screen of a cathode ray tube, a cold mirror, a low emissivity glass, an architectural glass, an anti-reflective panel glass, the screen of a cathode ray tube, a flexible film or a water vapour and oxygen barrier film.

- 10 -

6. A process as claimed in any one of the preceding claims wherein the sub-stoichiometric titanium dioxide has a resistivity of less than 0.1 ohm.cm.

5

7. A substrate which has been coated by a process as claimed in any one of claims 1 to 6.

8. A substrate as claimed in claim 7 which is a flexible film coated with sub-stoichiometric titanium dioxide,  $\text{TiO}_x$ , which has anti-static properties.

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9. A substrate as claimed in claim 7 wherein the coating is sub-stoichiometric titanium dioxide,  $\text{TiO}_x$ , which has a rutile crystalline structure.

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C23C14/08 C23C14/34 C04B35/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 096, no. 001, 31 January 1996 & JP 07 233469 A (ASAHI GLASS CO LTD), 5 September 1995, see abstract; tables 1,2 ---	1-5,7
A	DATABASE WPI Section Ch, Week 8925 Derwent Publications Ltd., London, GB; Class L03, AN 89-181603 XP002010492 & JP 01 118 807 A (HITACHI LTD) , 11 May 1989 see abstract -----	1-9

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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